Sustainable Solutions for Smart Life-Cycle Management (LCM) of Oils & Transformers: Diagnosis, Integrated Treatments and Case Histories for Corrosion Phenomena.

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Abstract - State of the art methods for diagnostics and selective depolarization of DBDS & Corrosion in mineral insulating oil, filling power transformers and shunt reactors, are described herewith. The target & priorities for 2013 are different type of corrosion - Tumiatti's Square:

- **C1 – DBDS & Corrosive Sulfur**
- **C2 – NON DBDS & Corrosive Sulfur**
- **C3 – SDBP & Corrosive Sulfur (SDBP – Sulfur Degradation By Products)**
- **C4 – NON Sulfur corrosion & Metal dissolution**

Diagnostic methods are based on the quantitative determination of a highly corrosive sulfur compound, Dibenzodisulfide (DBDS), and other corrosive sulfur compounds in unused and used insulating liquids, according to IEC 62697 – 2012, Part 1 and Part 2 (draft under completion). The subjectivity intrinsic to current standard test methods (ASTM D 1275 B and IEC 62535) for corrosive or potentially corrosive sulfur in insulating liquids is overcome through an objective approach for corrosiveness assessment. The quantitative determination of total corrosive sulfur (TCS) in insulating liquids permits an objective ranking of sulfur compounds according to their corrosiveness towards copper. Same Case Histories of sustainable solutions for the removal of DBDS & Corrosion, patented by Sea Marconi (Italy), are presented for the treatment of power transformer and Shunt Reactors. According to IEC 64422 Ed. 4-2013, such technology represents the Best Available Technique (BAT) and Best Environmental Practice (BEP) available worldwide, on site, in closed loop, on load (optional), without oil drainage.

Index Terms: **Dibenzodisulfide DBDS, Corrosive Sulfur, insulating liquids, Quantitative determination, Total Corrosive Sulfur – TCS, Selective Depolarization**

I. INTRODUCTION

Mineral insulating oils and other insulating fluids have a strategic role in electrical equipment (transformers, shunt reactors, tap changers, bushings, etc.) regarding generation, transmission, distribution and end-use of electrical power. Such equipment represent key assets for the oil and gas industry, mines, heavy industry, manufacturing, drinking water production and distribution, civil and defense infrastructures (hospitals, harbors, airports, railways, households, etc). As a consequence, diagnostics and depolarization activities are fundamental to protect the performance and reliability of equipment, in particular when corrosion phenomena can arise.

II. SCENARIO

Insulating liquids may contain corrosive sulfur compounds that, having detrimental effects on electrical equipment, such as transformer, have been investigated and classified in some macro classes that include elemental, inorganic and organic sulfur. The Total Sulfur Concentration (TCS) is related to the origin of the oil, the refining processes and the presence of additives. Insulating mineral oils are comprised of paraffinic and naphthenic bases, synthetic iso-paraffins, esters, poly α-olefins, poly alkylene glycol. Most of the additives act as electrostatic discharge depressants, metal deactivators, metal passivators, antioxidants, such as polysulfides and disulfides (e.g. dibenzyl disulfide - DBDS).

Some sulfur species that have antioxidant properties are corrosive and react with metal surfaces. Examples of these species are elemental sulfur, mercaptans and disulphide. Since their presence has been linked to failures of electrical equipment, the IEC standard for mineral insulating oils states that corrosive sulfur compounds shall not be present in unused and used insulating liquids (see IEC 60296 ed. 4 2012)[1].

Among the several corrosive compounds, one in particular, DBDS, is currently in the limelight, as its presence has been connected to cuprous sulphide formation on the surfaces of copper conductors under normal operating conditions of electrical equipment. Cuprous sulphide, which is a semiconductor, is held responsible for several short-circuit faults and windings deformation, through its build-up on paper [2-9].

Current standard test methods for detection of corrosive sulfur are ASTM D1275, methods A and B, and DIN 51353. In case of potentially corrosive sulfur, in used and unused insulating oil, the IEC 62535 standard is employed. All these methods are purely empirical and qualitative, as they depend on a visual and subjective perception of color [10-13], do not produce any quantitative result and are totally unreliable if a metal passivator is contained in the oil under investigation. As a matter of fact, in this latter case, a "False Negative" result can be produced, even if sulfur corrosive compounds are present. Contrarily, a "False Positive Result" can be returned when aging oils, acidic oils, undergoes the aforementioned test methods. Therefore, further confirmative analyses are required. IEC 62535 specifies that in case of doubts in the interpretation of the results from the inspection of paper analyzed by other methods (for example by SEM-EDX).

The International Electrotechnical Commission (IEC) Technical Committee 10 (TC 10) set up a working group (WG-37) aimed at developing methods for the unambiguous quantitative determination of corrosive sulfur compounds in unused and used insulating liquids. Because of the complexity of such determinations the test method was divided into three parts:

Part 1 – Test method for quantitative determination of the corrosive sulfur compound dibenzyldisulfide (DBDS).

Part 2 – Test methods for quantitative determination of total corrosive sulfur (TCS).

Part 3 – Test methods for quantitative determination of total thiols and disulfides (TMD) and other targeted corrosive sulfur species [14].

The analytical and diagnostic activities can achieve a full significance if contextualized in a broader scenario, where depolarization treatments are also included. Monitoring and maintaining the quality of insulating fluids and equipment is essential to guarantee a reliable functioning of electrical equipment. Therefore, codes of practice have been established by electrical power authorities, power companies and industries in many countries.

A few maintenance techniques are available for protecting metal surfaces from corrosion, such us adding metal passivators, replacing the oil or processing it through a Selective Depolarization treatment. In Table I an evaluation between oil replacement and Sea Marconi's Selective Depolarization is shown. It is evident that Selective Depolarization is economically and technically preferable to oil replacement. It does not require unused oil refilling, oil reconditioning, oil disposal, and guarantees the full recovery of chemical and physical properties. It's free from cross contaminations and can be performed keeping the transformer energized (On Load). In Table II the comparative evaluation between Selective Depolarization and simple Fuller's Hearth treatment (new and thermally regenerated) is also shown. Fuller's Hearth are totally unable to remove DBDS from the oil and when regenerated can impart corrosiveness to oil that are originally non-corrosive. Furthermore the regeneration steps represent an environmental issues being a possible source of POPs (PCBs, PCDDs-Dioxins, PCDFs-Furans, PCA, etc.), if emission control measures are not efficient.

Metal passivators additives, such as triazole derivatives (e.g. benzotraizole, toluyl triazole, Irgamet®30, Irgamet® 39), can only offer a temporary protection for metal from corrosion. Not only heat, but moisture and acidic conditions also, quickly degrade the mentioned molecules, impairing their passivating properties and exposing again the metal surfaces to the action of corrosive compounds. In Cigre document 378/2 – 2009 it is stated: "*..the addition of metal passivators is not a guarantee against failures. For instance, in Brazil, more than 200 shunt reactor oils in service were passivated (in most cases between ½ and 2 years after going into service). It has been reported that 9 of these units failed between one and 24 months after passivation…*" And in document 378/1- 2009 it is reported that "*there are a significant number of reports of increased hydrogen and carbon dioxide formation when the passivator is added to oil already in service".*

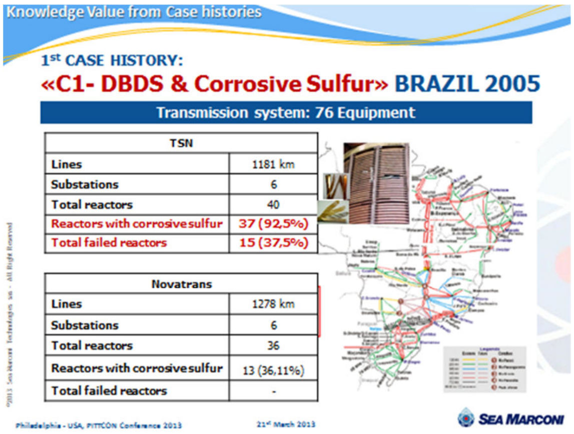
Furthermore triazole derivatives are classified as Harmful and Environmental Hazardous substances and can pose a serious threat to health and safety of workers (Suspected Carcinogenic) [15-16].

In this paper, methods and best practices for Life Cycle Management (LCM) of oils and transformers based on the State of the Art, IEC standards, Cigre Guidelines Best Available Techniques (BAT) and Best Environmental Practices (BEP) are presented together with a significant set of case histories [17].

One priority topic is represented by the "DBDS & Corrosion Free Program – Tumiatti's Square", a comprehensive diagnostic and processing tool, addressing four different types of corrosion:

- C1 – DBDS & Corrosive Sulfur
- C2 – NON DBDS & Corrosive Sulfur
- C3 – SDBP & Corrosive Sulfur (SDBP – Sulfur Degradation By Products)
- C4 – NON Sulfur corrosion & Metal dissolution

Some case histories are presented (Figures I- XV), for diagnostics and selective depolarization of DBDS, on site, closed loop, on-load (optional), according to CIGRE Report 378 [8] and IEC 60422 Ed. 4 – 2013 [18].



Knowledge Value from Case histories

1st CASE HISTORY:

«C1- DBDS & Corrosive Sulfur» BRAZIL 2005

Transmission system: 76 Equipment

TSN	
Lines	1181 km
Substations	6
Total reactors	40
Reactors with corrosive sulfur	37 (92,5%)
Total failed reactors	15 (37,5%)

Novatrans	
Lines	1278 km
Substations	6
Total reactors	36
Reactors with corrosive sulfur	13 (36,11%)
Total failed reactors	-

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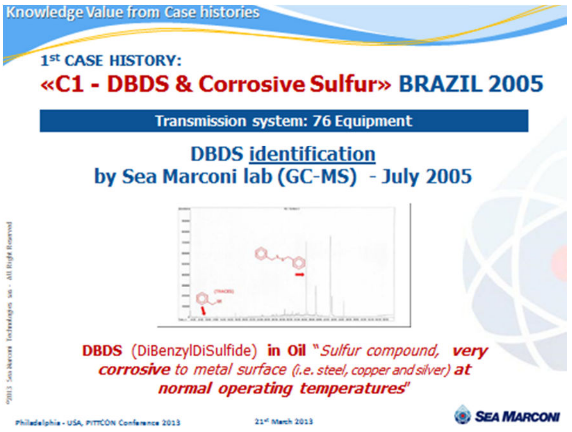
Fig. I - DBDS & Corrosion Sulfur (Brazil 2005): Shunt reactors 500 KV.



Knowledge Value from Case histories

1st CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» BRAZIL 2005

Transmission system: 76 Equipment

DBDS identification
by Sea Marconi lab (GC-MS) - July 2005

DBDS (DiBenzylDiSulfide) **in Oil** "*Sulfur compound,* ***very corrosive*** *to metal surface (i.e. steel, copper and silver)* ***at normal operating temperatures***"

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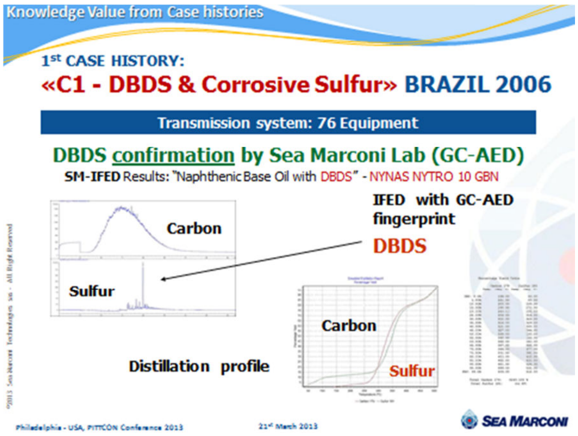
Fig. II - DBDS & Corrosion Sulfur (Brazil 2005): Shunt reactors 500 KV.



Knowledge Value from Case histories

1st CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» BRAZIL 2006

Transmission system: 76 Equipment

DBDS confirmation by Sea Marconi Lab (GC-AED)

SM-IFED Results: "Naphthenic Base Oil with DBDS" - NYNAS NYTRO 10 GBN

IFED with GC-AED fingerprint

DBDS

Carbon

Sulfur

Distillation profile

Carbon

Sulfur

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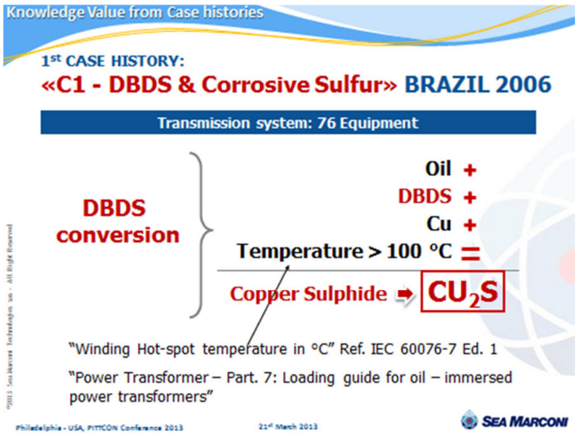
Fig. III - DBDS & Corrosion Sulfur (Brazil 2005): Shunt reactors 500 KV.



Knowledge Value from Case histories

1st CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» BRAZIL 2006

Transmission system: 76 Equipment

DBDS conversion

Oil +
DBDS +
Cu +
Temperature > 100 °C =

Copper Sulphide ➡ CU_2S

"Winding Hot-spot temperature in °C" Ref. IEC 60076-7 Ed. 1

"Power Transformer – Part. 7: Loading guide for oil – immersed power transformers"

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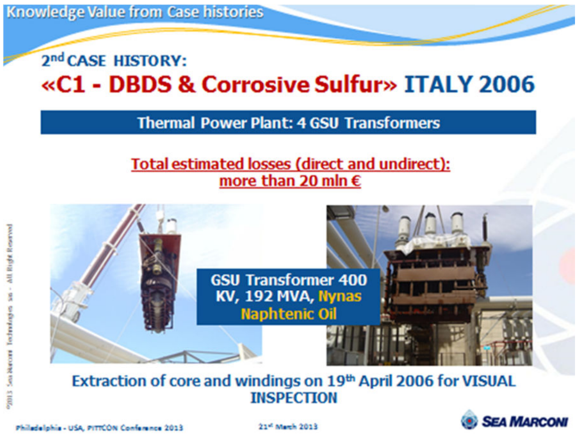
Fig. IV - DBDS & Corrosion Sulfur (Brazil 2005): Shunt reactors 500 KV.



Knowledge Value from Case histories

2nd CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» ITALY 2006

Thermal Power Plant: 4 GSU Transformers

Total estimated losses (direct and undirect):
more than 20 mln €

GSU Transformer 400 KV, 192 MVA, Nynas Naphtenic Oil

Extraction of core and windings on 19th April 2006 for VISUAL INSPECTION

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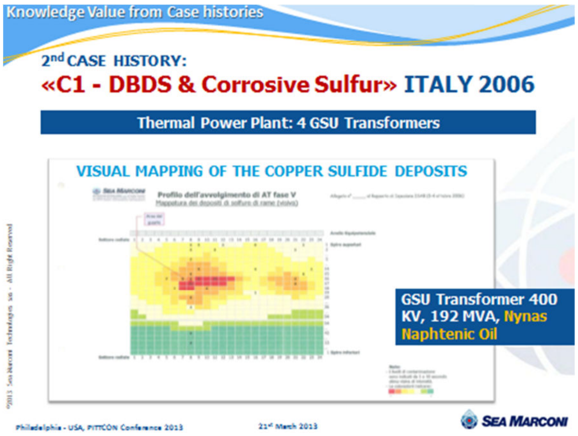
Fig. V - DBDS & Corrosion Sulfur (Italy 2006): GSU Transformer 400 KV.



Knowledge Value from Case histories

2nd CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» ITALY 2006

Thermal Power Plant: 4 GSU Transformers

VISUAL MAPPING OF THE COPPER SULFIDE DEPOSITS

GSU Transformer 400 KV, 192 MVA, Nynas Naphtenic Oil

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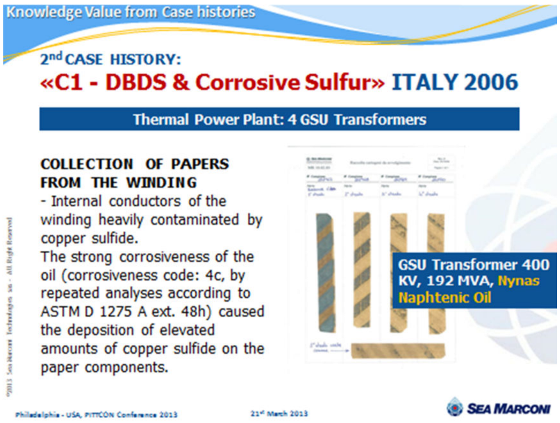
Fig. VI - DBDS & Corrosion Sulfur (Italy 2006): GSU Transformer 400 KV.



Knowledge Value from Case histories

2nd CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» ITALY 2006

Thermal Power Plant: 4 GSU Transformers

COLLECTION OF PAPERS FROM THE WINDING

- Internal conductors of the winding heavily contaminated by copper sulfide.

The strong corrosiveness of the oil (corrosiveness code: 4c, by repeated analyses according to ASTM D 1275 A ext. 48h) caused the deposition of elevated amounts of copper sulfide on the paper components.

GSU Transformer 400 KV, 192 MVA, Nynas Naphtenic Oil

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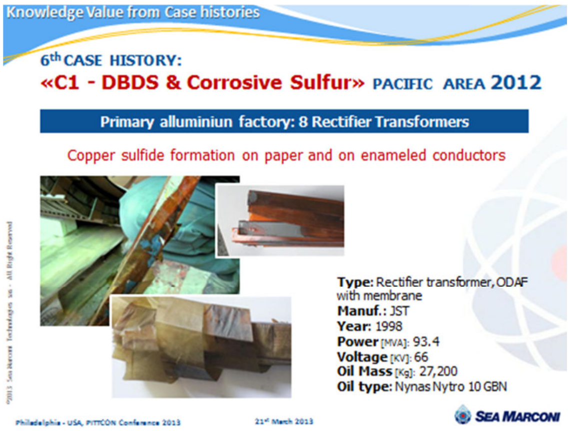
Fig. VII - DBDS & Corrosion Sulfur (Italy 2006): GSU Transformer 400 KV.



Knowledge Value from Case histories

6th CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» PACIFIC AREA 2012

Primary alluminiun factory: 8 Rectifier Transformers

Copper sulfide formation on paper and on enameled conductors

Type: Rectifier transformer, ODAF with membrane
Manuf.: JST
Year: 1998
Power [MVA]: 93.4
Voltage [KV]: 66
Oil Mass [Kg]: 27,200
Oil type: Nynas Nytro 10 GBN

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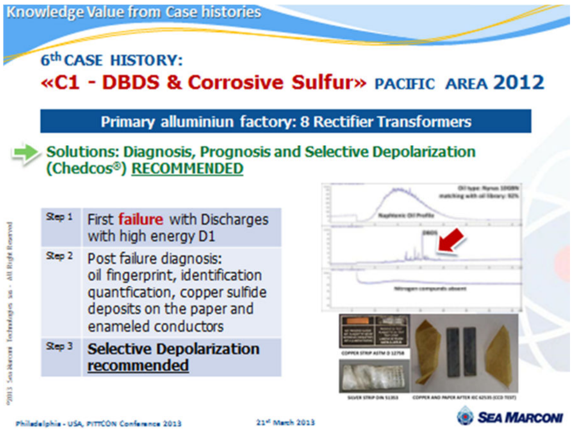
Fig. VIII - DBDS & Corrosion Sulfur (Pacific Area 2012): Rectifier Transformers



Knowledge Value from Case histories

6th CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» PACIFIC AREA 2012

Primary alluminiun factory: 8 Rectifier Transformers

Solutions: Diagnosis, Prognosis and Selective Depolarization (Chedcos®) RECOMMENDED

Step 1	First failure with Discharges with high energy D1
Step 2	Post failure diagnosis: oil fingerprint, identification quantfication, copper sulfide deposits on the paper and enameled conductors
Step 3	**Selective Depolarization recommended**

Naphtenic Oil Profile
DBDS
Nitrogen compounds absent
COPPER STRIP ASTM D 1275B
SILVER STRIP DIN 51353
COPPER AND PAPER AFTER IEC 62535 (CCD TEST)

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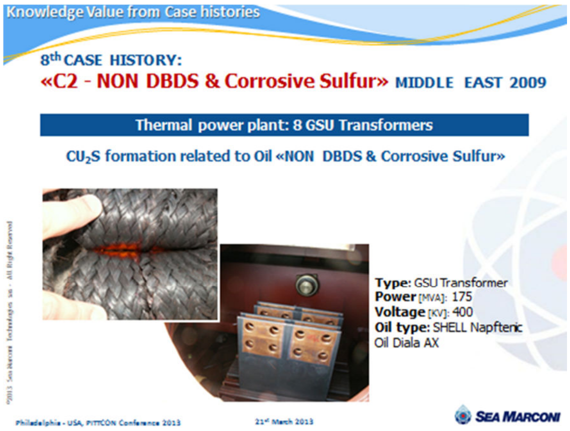
Fig. IX - DBDS & Corrosion Sulfur (Pacific Area 2012): Rectifier Transformers



Knowledge Value from Case histories

8th CASE HISTORY:

«C2 - NON DBDS & Corrosive Sulfur» MIDDLE EAST 2009

Thermal power plant: 8 GSU Transformers

CU_2S formation related to Oil «NON DBDS & Corrosive Sulfur»

Type: GSU Transformer
Power [MVA]: 175
Voltage [KV]: 400
Oil type: SHELL Napftenic Oil Diala AX

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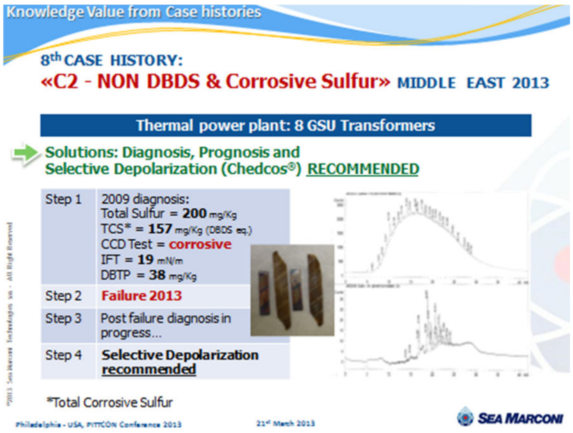
Fig. X - NON DBDS & Corrosion Sulfur (Middle East 2009): GSU Transformer 400 KV



Knowledge Value from Case histories

8th CASE HISTORY:

«C2 - NON DBDS & Corrosive Sulfur» MIDDLE EAST 2013

Thermal power plant: 8 GSU Transformers

Solutions: Diagnosis, Prognosis and Selective Depolarization (Chedcos®) RECOMMENDED

Step 1	2009 diagnosis: Total Sulfur = **200** mg/Kg TCS* = **157** mg/Kg (DBDS eq.) CCD Test = **corrosive** IFT = **19** mN/m DBTP = **38** mg/Kg
Step 2	**Failure 2013**
Step 3	Post failure diagnosis in progress...
Step 4	**Selective Depolarization recommended**

*Total Corrosive Sulfur

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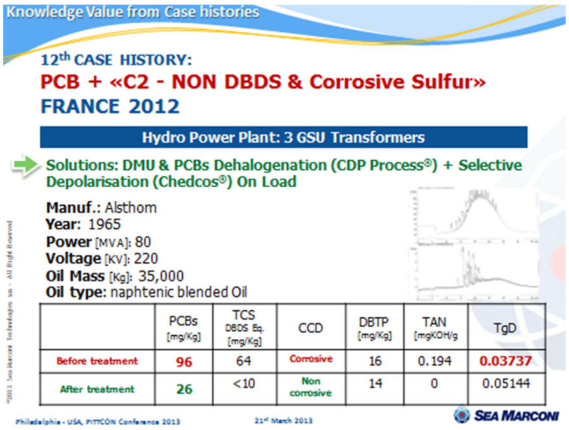
Fig. XI - NON DBDS & Corrosion Sulfur (Middle East 2009): GSU Transformer 400 KV



Knowledge Value from Case histories

12th CASE HISTORY:

PCB + «C2 - NON DBDS & Corrosive Sulfur»

FRANCE 2012

Hydro Power Plant: 3 GSU Transformers

Solutions: DMU & PCBs Dehalogenation (CDP Process®) + Selective Depolarisation (Chedcos®) On Load

Manuf.: Alsthom
Year: 1965
Power [MVA]: 80
Voltage [KV]: 220
Oil Mass [Kg]: 35,000
Oil type: naphtenic blended Oil

	PCBs [mg/Kg]	TCS DBDS Eq. [mg/Kg]	CCD	DBTP [mg/Kg]	TAN [mgKOH/g	TgD
Before treatment	96	64	Corrosive	16	0.194	0.03737
After treatment	26	<10	Non corrosive	14	0	0.05144

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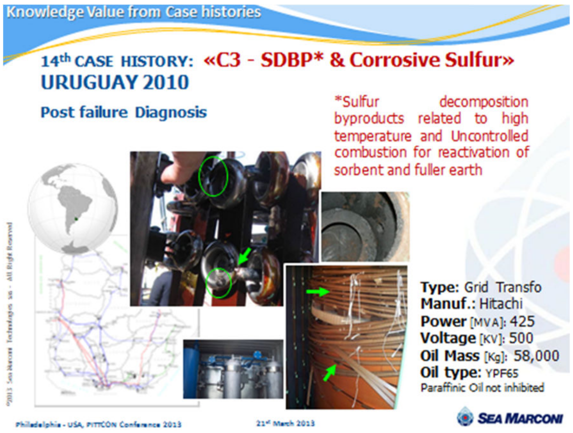
Fig. XII - NON DBDS & Corrosion Sulfur (France 2012): GSU Transformer 220 KV



Knowledge Value from Case histories

14th CASE HISTORY: **«C3 - SDBP* & Corrosive Sulfur»**

URUGUAY 2010

Post failure Diagnosis

*Sulfur decomposition byproducts related to high temperature and Uncontrolled combustion for reactivation of sorbent and fuller earth

Type: Grid Transfo
Manuf.: Hitachi
Power [MVA]: 425
Voltage [KV]: 500
Oil Mass [Kg]: 58,000
Oil type: YPF65
Paraffinic Oil not inhibited

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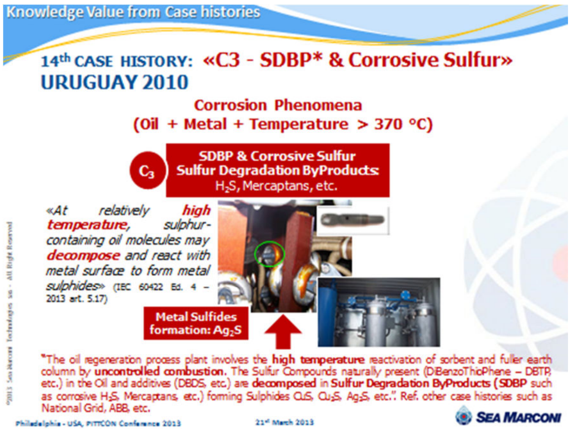
Fig. XIII - SDBP & Corrosion Sulfur (Uruguay 2010): Grid Transfo 500 KV



Knowledge Value from Case histories

14th CASE HISTORY: **«C3 - SDBP* & Corrosive Sulfur»**

URUGUAY 2010

Corrosion Phenomena
(Oil + Metal + Temperature > 370 °C)

C_3 **SDBP & Corrosive Sulfur**
Sulfur Degradation ByProducts:
H_2S, Mercaptans, etc.

*«At relatively **high temperature**, sulphur-containing oil molecules may **decompose** and react with metal surface to form metal sulphides»* (IEC 60422 Ed. 4 – 2013 art. 5.17)

Metal Sulfides formation: Ag_2S

*The oil regeneration process plant involves the **high temperature** reactivation of sorbent and fuller earth column by **uncontrolled combustion**. The Sulfur Compounds naturally present (DiBenzoThioPhene – DBTP, etc.) in the Oil and additives (DBDS, etc.) are **decomposed** in **Sulfur Degradation ByProducts (SDBP** such as corrosive H_2S, Mercaptans, etc.) forming Sulphides CuS, Cu_2S, Ag_2S, etc.". Ref. other case histories such as National Grid, ABB, etc.

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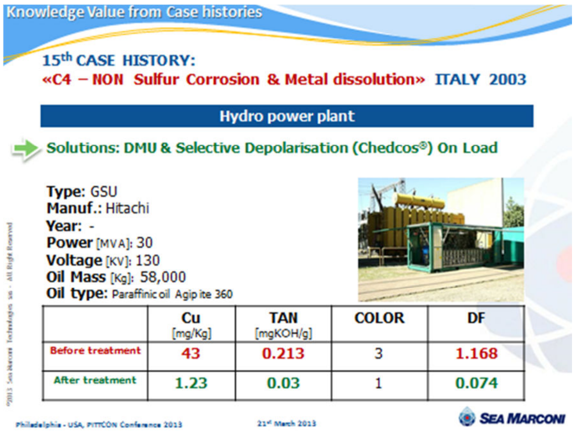
Fig. XIV - SDBP & Corrosion Sulfur (Uruguay 2010): Grid Transfo 500 KV



Knowledge Value from Case histories

15th CASE HISTORY:

«C4 – NON Sulfur Corrosion & Metal dissolution» ITALY 2003

Hydro power plant

Solutions: DMU & Selective Depolarisation (Chedcos®) On Load

Type: GSU
Manuf.: Hitachi
Year: -
Power [MVA]: 30
Voltage [KV]: 130
Oil Mass [Kg]: 58,000
Oil type: Paraffinic oil Agip ite 360

	Cu [mg/Kg]	TAN [mgKOH/g]	COLOR	DF
Before treatment	43	0.213	3	1.168
After treatment	1.23	0.03	1	0.074

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Fig. XV - NON Sulfur Corrosion & Metal dissolution (Italy 2003): GSU Transfo 130 KV

TABLE I. COMPARISON BETWEEN SEA MARCONI'S SELECTIVE DEPOLARIZATION AND OIL REPLACEMENT.

Key Factors	**Sea Marconi Closed loop treatment**	**Replacement of Oil**
On-Load Operation	Yes ✓	✗ No Off-Load for Draining and Refilling
Requirement of Unused Oil	No ✓	✗ Yes 125%/150% of original mass of oil
Compatibility of Unused Oil vs original	Safety ✓	⚠ Warning base Oil, additives, others
Recovery: Physical Properties KV, DGA, H_2O	Yes ✓	⚠ Warning only after reconditioning of Unused Oil in closed loop §11.2.3 (IEC 60422 Ed. 4 2013)
Recovery: Chemical Properties TAN, DF, IFT	Yes ✓	⚠ Warning only after reconditioning + reclam. treatments of Unused oil in closed loop §11.3 (IEC 60422 Ed. 4 2013)
Removal: DBDS & Corrosive Sulfur	Yes ✓	⚠ Warning only if initial DBDS is < 80 mg/Kg or reclamation with special adsorbent
Desludging & Dehydration Solid Insulation	Yes ✓	⚠ Warning only after reconditioning + reclamation of Unused oil in closed loop §11.3 (IEC 60422 Ed. 4 2013)
Decontamination: Dissolved Metals	Yes ✓	⚠ Warning only after reclamation with special adsorbent. Initial value 8/10 times higher than target limit
Dehalogenation: PCBSs/POPs in Oils	Yes ✓	⚠ Warning only if initial PCBs is 8/10 times higher than the target limit
Self-cleaning unit from: DBDS, PCBs/POPs	Yes ✓	✗ No cross contamination
Cross contamination by DBDS, PCBs/POPs	Safety ✓	⚠ Warning depending on the used oil mainly in the solid insulation
Partial Discharges: air bubble & moisture	Safety ✓	⚠ Warning especially for wet insulation
Environmental Risks for Oil handling	Safety ✓	⚠ Warning high logistical impact
Oil & PCBs Waste disposal	No ✓	✗ Yes especially if PCBs is higher than limit

TABLE II. COMPARISON BETWEEN SEA MARCONI'S SELECTIVE DEPOLARIZATION AND FULLER'S HARTH TREATMENT.

Key Factors	**DMU & Integrated Treatments Sea Marconi Patented**	Treatment with typical Fuller Earth	Treatment with typical Fuller Earth and regeneration > 600-700 °C
Recovery: Physical Properties KV, DGA, H_2O	✓ Yes	✓ Yes	✓ Yes
Recovery: Chemical Properties TAN, DF, IFT	✓ Yes	✓ Yes	✓ Yes
Removal: DBDS & Corrosive Sulfur	✓ Yes	✗ No	✗ No
Decontamination: Dissolved Metals	✓ Yes	✗ No	✗ No
Dehalogenation: PCBs/POPs in Oils	✓ Yes	✗ No	✗ No
Classification: BAT/BEP - Best Available Techniques/ Best Environmental Practices (PCBs/POPs)	✓ Yes	✗ No	✗ No
Self-cleaning unit from: DBDS, PCBs/POPs	✓ Yes	✗ No	✗ No
Cross contamination by DBDS, PCBs/POPs	🛡 Safety	⚠ Danger	⚠ Danger
Corrosion by Sulfur Degradation byProducts (SDBP) as H_2S, RSH etc. due to high temperature	🛡 Safety	🛡 Safety	⚠ Danger
Dioxins Emissions (PCDDs, PCDFs) due to high temperature degradation by products	🛡 Safety	🛡 Safety	⚠ Danger

III. TYPICAL PROJECT DESCRIPTION

The typical project starts with the diagnostic activities to classify type of corrosion phenomena for power transformers, shunt reactor and strategic equipment. The Dibenzyl Disulfide (DBDS), is one of the most commonly occurring corrosive sulfur compounds in mineral insulating oils. Other type of corrosion markers have been selected for integrated diagnostics. As stated above, corrosive sulfur compounds react with copper conductors in electrical power apparatus, resulting in the formation of copper sulfide. The latter, which is a conducting compound, diffuses into the oil-impregnated-paper tapes adjacent to the conductor, leading to the loss of the dielectric strength and, subsequently, to a short circuit between adjacent turns or towards ground (Figure XVI). The risk of failure is increased by high temperature, load and voltage levels. Over the last years, several failures in shunt reactors and power transformers worldwide have been attributed to the presence of DBDS & Corrosive Sulfur.

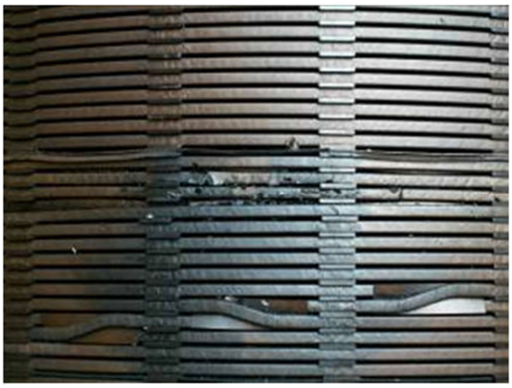


Fig. XVI. A failure related to corrosive sulfur formation

The diagnostic report assess the corrosiveness classification (types and priority), in order to implement the most efficient countermeasures able to remove DBDS & Corrosion and prevent and/or mitigate the failures risks.

Performing the analysis of the single parameter of interest (e.g. DBDS) without acquiring a comprehensive understanding of the real situation of the electrical equipment can lead to serious problem during and after treatment operation. That is the reason why a preventive diagnostic approach enables a safe and effective planning of depolarization activities

Adding of metal passivators, oil replacement and Selective Depolarization treatment were all examined with regard to technical, economic and environmental aspects.

Sea Marconi's diagnostic expertise (since 1968) and its Selective Depolarization technique were selected, as the best cost-effective approach [19]. The Selective Depolarization process is performed on site, by a mobile depolarization units (DMU) which performs a continuous closed-loop circulation of the oil (see Figures XVII-XXIII). Passing through the DMU, the oil is heated and circulated through a series of percolation column, containing a mixture of active chemical reagents (Sea Marconi patent) and a suitable mixture of sorbents materials. A vacuum dehydrator ensures the removal of moisture and gases present in the oil or resulting from the chemical reaction. If needed, the process can be performed with the transformer energized, without interruption of the service during the treatment (On Load).

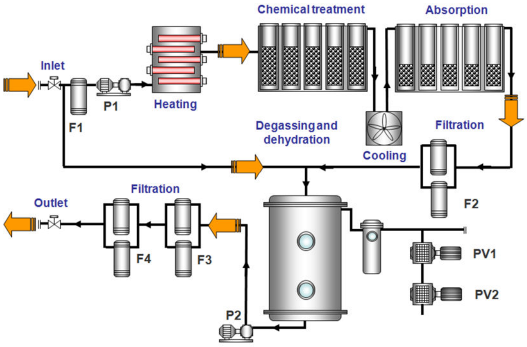
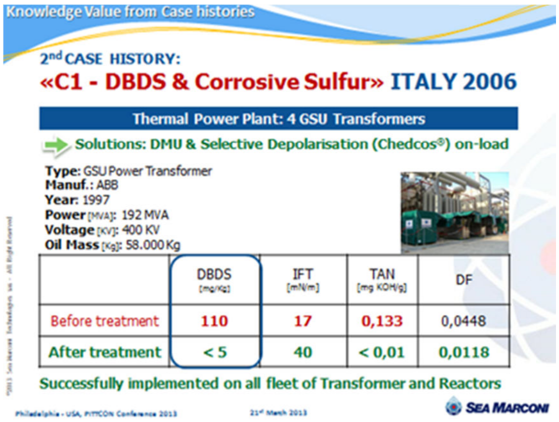


Fig. XVII. Hydraulic flow diagram of the depolarization unit

The project expertise involves more than 300 large HV power transformers and shunt reactors, located in several countries in Europe, South America, Middle East, etc.



Knowledge Value from Case histories

2nd CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» ITALY 2006

Thermal Power Plant: 4 GSU Transformers

Solutions: DMU & Selective Depolarisation (Chedcos®) on-load

Type: GSU Power Transformer
Manuf.: ABB
Year: 1997
Power [MVA]: 192 MVA
Voltage [KV]: 400 KV
Oil Mass [Kg]: 58.000 Kg

	DBDS [mg/Kg]	IFT [mN/m]	TAN [mg KOH/g]	DF
Before treatment	110	17	0,133	0,0448
After treatment	< 5	40	< 0,01	0,0118

Successfully implemented on all fleet of Transformer and Reactors

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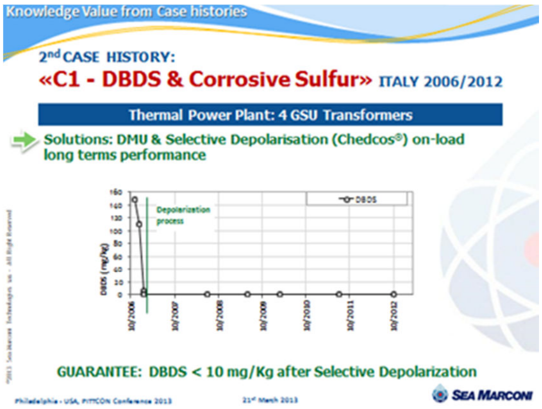
Fig. XVIII. DMU & Selective Depolarisation (Italy 2006) : shunt reactors and GSU transformers 400 KV



Knowledge Value from Case histories

2^{nd} CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» ITALY 2006/2012

Thermal Power Plant: 4 GSU Transformers

Solutions: DMU & Selective Depolarisation (Chedcos®) on-load long terms performance

GUARANTEE: DBDS < 10 mg/Kg after Selective Depolarization

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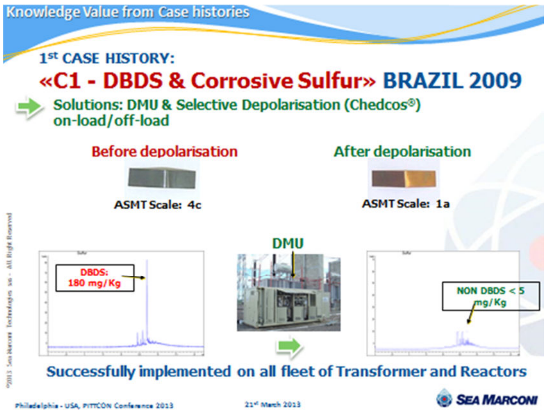
Fig. XIX. DMU & Selective Depolarisation (Brazil 2009) : shunt reactors and GRID transformers 500 KV



Knowledge Value from Case histories

1^{st} CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» BRAZIL 2009

Solutions: DMU & Selective Depolarisation (Chedcos®) on-load/off-load

Before depolarisation
ASMT Scale: 4c
After depolarisation
ASMT Scale: 1a
DMU
DBDS: 180 mg/Kg
NON DBDS < 5 mg/Kg

Successfully implemented on all fleet of Transformer and Reactors

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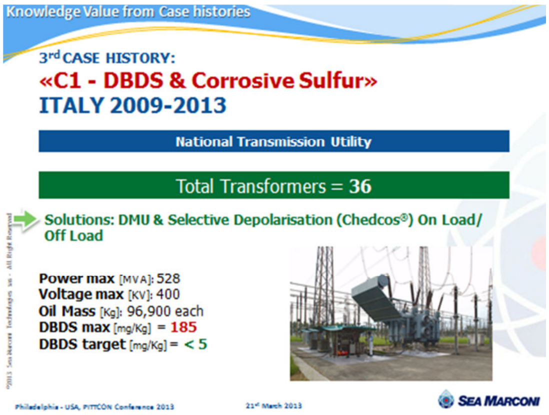
Fig. XX. DMU & Selective Depolarisation (Brazil 2009) : shunt reactors and GRID transformers 500 KV



Knowledge Value from Case histories

3^{rd} CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur»
ITALY 2009-2013

National Transmission Utility

Total Transformers = 36

Solutions: DMU & Selective Depolarisation (Chedcos®) On Load/ Off Load

Power max [MVA]: 528
Voltage max [KV]: 400
Oil Mass [Kg]: 96,900 each
DBDS max [mg/Kg] = 185
DBDS target [mg/Kg] = < 5

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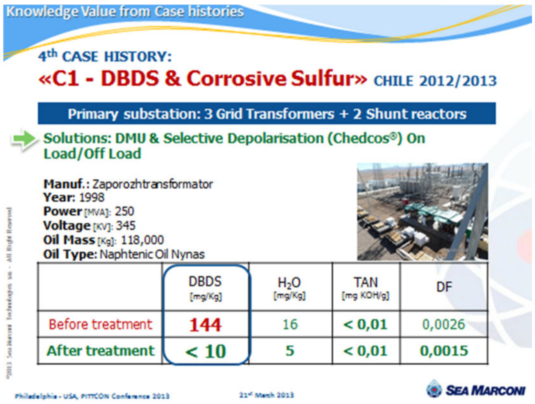
Fig. XXI. DMU & Selective Depolarisation (Italy 2009-2013) : shunt reactors and GRID transformers 400 KV



Knowledge Value from Case histories

4^{th} CASE HISTORY:

«C1 - DBDS & Corrosive Sulfur» CHILE 2012/2013

Primary substation: 3 Grid Transformers + 2 Shunt reactors

Solutions: DMU & Selective Depolarisation (Chedcos®) On Load/Off Load

Manuf.: Zaporozhtransformator
Year: 1998
Power [MVA]: 250
Voltage [KV]: 345
Oil Mass [Kg]: 118,000
Oil Type: Naphtenic Oil Nynas

	DBDS [mg/Kg]	H_2O [mg/Kg]	TAN [mg KOH/g]	DF
Before treatment	144	16	< 0,01	0,0026
After treatment	< 10	5	< 0,01	0,0015

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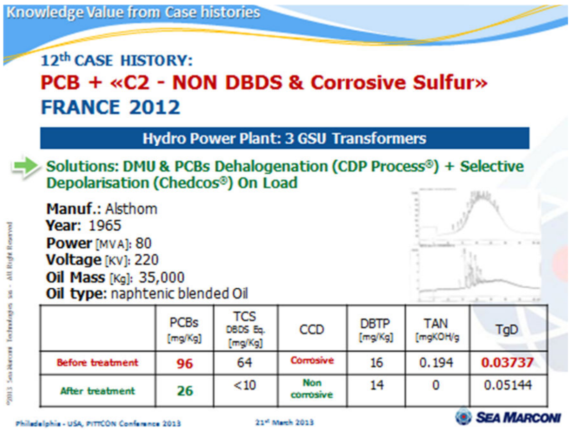
Fig. XXII. DMU & Selective Depolarisation (Chile 2012-2013) : shunt reactors and GRID transformers 345 KV



Knowledge Value from Case histories

12^{th} CASE HISTORY:

PCB + «C2 - NON DBDS & Corrosive Sulfur»
FRANCE 2012

Hydro Power Plant: 3 GSU Transformers

Solutions: DMU & PCBs Dehalogenation (CDP Process®) + Selective Depolarisation (Chedcos®) On Load

Manuf.: Alsthom
Year: 1965
Power [MVA]: 80
Voltage [KV]: 220
Oil Mass [Kg]: 35,000
Oil type: naphtenic blended Oil

	PCBs [mg/Kg]	TCS DBDS Eq. [mg/Kg]	CCD	DBTP [mg/Kg]	TAN [mgKOH/g	TgD
Before treatment	96	64	Corrosive	16	0.194	0.03737
After treatment	26	<10	Non corrosive	14	0	0.05144

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Fig. XXIII. DMU & Selective Depolarisation (France 2012) : shunt reactors and GSU transformers 220 KV.

IV. PROCESS DESCRIPTION

The Selective Depolarization method is based on a chemical reaction that increases the polarity of the corrosive sulfur compounds that can be subsequently removed by absorption. Not only are DBDS and other polar corrosive sulfur compounds adsorbed, but also other non-sulfur polar species. [20].

The chemical solid reagents are blends of inert aluminum-silicate support and active chemical reagents, intimately mixed to form a mixture with an average particle size between 0.5 and 1 mm. The absorption solid reagents are suitable mixtures of clay, soils and other sorbents with high active surface. The first step, which modifies the chemical nature of undesired substances increasing their polarity, takes place between 80 and 90 °C; secondly, the oil is cooled down to 55-60 °C for the following absorption step, where polar substances are retained on the active surface.

A vacuum dehydrator ensures the removal of moisture and gases if present in the oil or resulting from the chemical reactions.

Spent reagents and sorbent materials are not reactivated by uncontrolled combustion during the treatment, avoiding the risk of generating other potentially corrosive compounds during the reactivation process (Ex. H_2S mercaptans, elemental sulfur, etc.). Additional unit are develop by Sea Marconi for reactivation of the solid materials and reagents without combustion , for recovery of materials (oil, solid reagents and absorbent) , “zero-waste” approach and “zero dangerous emissions”.

V. FIELD APPLICATION

The Selective Depolarization process was performed on site, by a mobile depolarization unit (DMU) which was connected to the transformer tank to realize a continuous closed circulation of the oil.

Passing through the DMU, the oil is heated and circulated through a series of percolation columns, containing the active chemical reagents and a suitable mixture of clay and sorbent materials.

The treatment was performed keeping the transformer in off-load mode and grounded (even if the technology is suitable to be operated with the transformer energized, without interruption of the service during the treatment).

Property	**Unit**	**Initial Value**	**Final Value**	**Required Value**
DBDS	mg/kg	137	6	< 10
TCS	mg/kg	28	< 2	2
Corrosive Sulfur (IEC 62535)		Corrosive	Non Corrosive	Non Corrosive
Water	mg/kg	3	2	< 5
Breakdown V	KV	69	74.1	> 70
Acidity	mgKOH/g	< 0.01	< 0.01	< 0.01
DDF		0.00408	0.00401	
Particles	ISO	15/13/9	14/12/9	
IFT	mN/m	31.6	41.3	
Total gases	%	4.17	0.3	
Irgamet39	mg/kg	17	< 3	

The technology has been operated by specialized technical personnel from the supplier (Sea Marconi).

The total duration of the process, for each transformer, was around 5-10 cycles (about 5-30 days depending of the size of transformers, oil mass, oil degradation, type and contaminants concentration and/or interferences, On-Load and Off-Load operation).

VI. LABORATORY & DIAGNOSTIC ACTIVITIES

A complete Diagnosis was performed by Sea Marconi on the oils sampled from the electrical devices. All fundamental chemical and physical properties were determined before and at the end of the depolarization processes (DBDS, H_2O, Particle, Corrosion, etc). The DBDS concentration was also monitored on site during the treatment by means of the SM-TCS test [20] (TCS and $DBDS_{eq}$ values- Fig. XXV and XXVI).

Fig. XXIV. A view of Sea Marconi’s lab, Italy

VII. TYPICAL RESULTS AND BENEFITS

Typical results example of the Selective Depolarization Treatments are describe.
For a typical GRID transformer, 250 MVA, 345/220 kV, was filled with 118.000 Kg of naphthenic oil containing 137 mg Kg^{-1} of DBDS. The DBDS concentration was cut down to less than 10 mg Kg^{-1} and the oil was classified “Non Corrosive” according to IEC 62535 and ASTM D 1275 B methods, after treatment. The dielectric, chemical and physical properties of the oil were also improved (Table III).

TABLE III. INITIAL AND FINAL VALUES OF MAIN ANALYTICAL PARAMETER FROM THE OIL IN THE FIRST TRANSFORMER

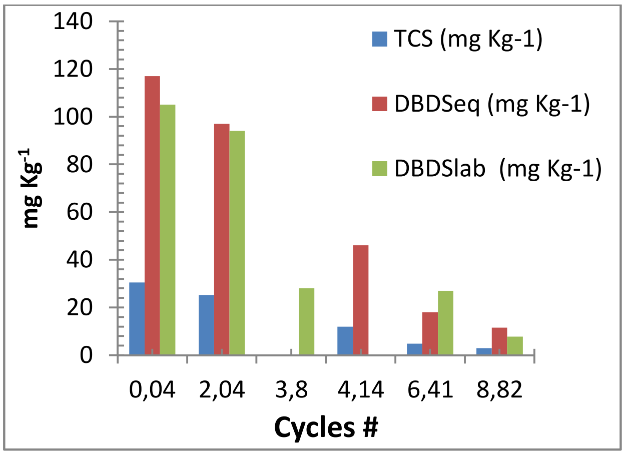

Fig. XXV. DBDS concentration as a function of the number of cycles. Comparison between on-site determination (TCS and DBDSeq) and laboratory analysis (DBDSlab). DBDSeq and DBDSlab concentration.

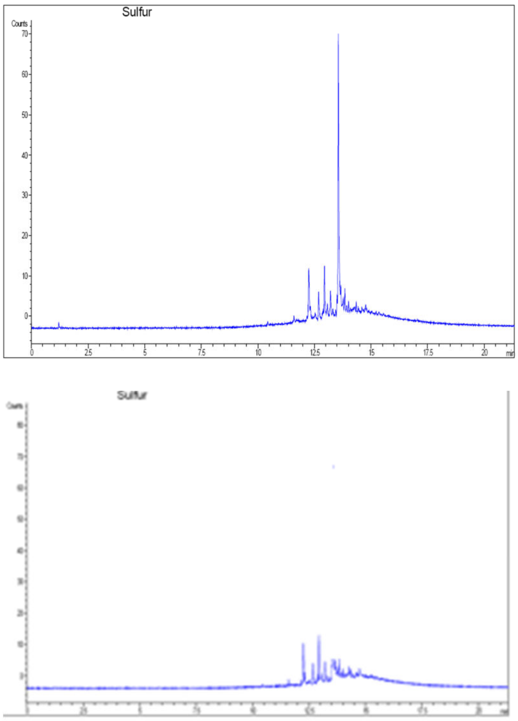

Fig. XXVI. DBDS determination by GC-AED. Before (chromatogram above) and after treatment (chromatogram below)- according to IEC 62697-2012 -Part1.

The benefit is to avoid economic losses, which can easily exceed a million dollars/euros for energy loss, fines and costs of repositioning or repairing of power transformer, shunt reactor and strategic equipment.

VII. CONCLUSION

The DBDS & Corrosion Free Program has demonstrated to be successful in view of the fact that is based on an efficient and reliable integration between the Best Available (BAT) diagnostic and treatment activities, in compliance with the Best Environmental Practices (BEP). Severe environmental conditions confirmed, more than ever, that a skillful management of laboratory, planning and processing activities is essential. Furthermore, the necessity of offering an efficacious and foolproof service in a far and barren site has required a good deal of inventiveness to overcome logistical, technical and, sometimes, unexpected problems. The Selective Depolarization treatment has proved to be an effective technique to remove DBDS and corrosive compounds from mineral insulating oils and to reduce the associated risk of shortening the life of equipment, avoiding large investments for repair or replacement and costs related to loss of production.

Therefore, Life Cycle Management (LCM) is an indispensable tool for the prevention and/or mitigation of direct and indirect losses and associated risks for workers, assets, public health and environment, that can arise from human errors, malfunctioning, or failures of the equipment and be a source of fires and/or spillage of hazardous substances (Oils, PCA, etc.) and Persistent Organic Pollutants (POPs; PCBs, etc.).

V REFERENCES

[1] IEC 60296:2012, Fluids for electrotechnical applications – Unused mineral insulating oils for transformers and switchgear.

[2] Lewand R.L., Corrosive Sulfur in Transformer Systems, Chemist’s perspective, DOBLE ENGINEERING COMPANY - NETA WORLD, U.S.A., 2003.

[3] Wilson A.C.M., *Insulating Liquids: their use, manufacture and properties*, IEEE, New York and UK, 1980.

[4] Lewand R. L., *The Negative Effects of Corrosive Sulfur on Transformer Components*, DOBLE ENGINEERING COMPANY - NETA WORLD, U.S.A., 2004.

[5] Scatiggio F., *Corrosive Sulfur*, Proceedings of IEC TC 10 Plenary meeting, Cape Town, 2005.

[6] Tumiatti V., Maina R., Scatiggio F., Pompili M., and R. Bartnikas, *Corrosive Sulfur in mineral oils: its detection and correlated transformer failures*– IEEE International Symposium on Electrical Insulation, Toronto (Canada), 2006.

[7] Maina, R., Scatiggio, F., Kapila, S., Tumiatti, V., Tumiatti, M. and Pompili, M., *Dibenzyl disulfide (DBDS) contaminant in used and unused mineral insulating oils. CIGRE SC2, 2006* (http://www.cigre-a2.org).

[8] CIGRE Technical Report 378: *Copper Sulphide in Transformer Insulation*, April 2009.

[9] K. Anderson, S. Kapila, V. Flanigan, V. Tumiatti, R. Maina, and M. Tumiatti, *Determination of corrosive sulfur species in mineral insulating oils using GC – AED, GC-MS-MS – FTMS.* Abstract No. 800-2; presented at PittCon 2009, Chicago, IL, March, 2009.

[10] IEC 62535:2008, insulating liquids – Test method for detection of potentially corrosive sulphur in used and unused insulating oil.

[11] ASTM D1275, Methods A and B, Standard test method for corrosive sulphur in electrical insulating oils.

[12] ASTM D130, Standard test method for corrosiveness to copper from petroleum products by copper strip test.

[13] DIN 51353, Testing of insulating oils: detection of corrosive sulphur; silver strip test.

[14] Tumiatti V., Roggero C.M., Kapila S., et. al., IEC 62697 – 2012: State of the Art Methods for Quantification of DBDS and Other Corrosive Sulfur Compounds in Unused and Used Insulating Liquids, IEEE transactions on dielectrics and electrical insulation, Vol 19, Issue 5, pag 1633 10/01/2012

[15] Stouten, H, Rutten, AJL, van de Gevel, IA, De Vrijer, F, 2000. Nordic Expert Group for Criteria Documentation of Health Risks from Chemicals and the Dutch Expert Committee on Occupational Standards: 126. 1,2,3-Benzotriazole. National Institute for Working Life. Stockholm, Sweden

[16] National Cancer Institute Technical Report Series No. 881978 “Bioassay of 1H- Benzotriazole for possible carcinogenicity CAS No. 95-14-7 “ NCI-CG-TR-88 - U.S. department of Health, Education, and Welfare Public Health Service National Institutes of Health

[17] Tumiatti V., Smart Life Cycle Management of Oils & Equipment Pittcon 2013, Philadelphia.

[18] IEC 60422 ed4.0 Mineral insulating oils in electrical equipment - Supervision and maintenance guidance. Pub. Date 2013-01-10

[19] V. Tumiatti, R. Maina, F. Scatiggio, M. Pompili and R. Bartnikas, “In service reduction of corrosive sulfur compounds in insulating mineraloils”, ISEI 2008.

[20] Tumiatti V. Kapila S. Roccero C.M., et al. Integrated Methods for corrosivity, ageing and fingerprinting determination, as well as diagnosis, decontamination, depolarization and detoxification of oils, Int. Pub. Num. WO 2010/070590 A1, 24 June 2010.

Vander Tumiatti is the Founder and Owner of SEA MARCONI TECHNOLOGIES (since 1968), Torino, Italy, an international company that is involved in research, technologies, products, and services for energy & environment. He has developed BAT & BEP Sustainable Solutions for Life Cycle Management (LCM) of insulting liquids & transformers focalized on inventory, control, diagnosis, decontamination, depolarization (DBDS, TCS, Polar Compounds) end dehalogenation /detoxification (PCBs/POPs).

He has more than 40 international patents and is the author of many international technical and scientific publications. He has been the Assistant Secretary of IEC TC10 since 2000. He is also a member of several international groups, with major participation in technical normative activities (CEN, IEC, CIGRE ,IEEE).

2009 June -"1906 Award", Award IEC.

Since 2001 **Riccardo Maina** works for Sea Marconi Technologies, an Italian Company leader in diagnostic and maintenance of insulating liquids. As Laboratory Manager of Sea Marconi he developed new analytical methods for oil analysis, diagnostics and decisional algorithms for test interpretation, software for data mining and LCA. He's member of the Italian IEC TC10 National Committee since 2002, and is actively participating to several WGs and MTs of IEC TC10 and Cigre SC D1 and A2, dealing with analytical methods (particles, DGA, acidity, additives, metals), maintenance guides, guides for interpretation and diagnostics (oil degradation, DGA, thermal life of cellulose).
Riccardo Maina is author of papers on diagnostics, transformers LCA, corrosive sulphur.